



# Removal of pendimethalin from soil washing effluents using electrolytic and electro-irradiated technologies based on diamond anodes



Perla T. Almazán-Sánchez<sup>a</sup>, Salvador Cotillas<sup>b</sup>, Cristina Sáez<sup>c</sup>, Marcos J. Solache-Ríos<sup>d</sup>, Verónica Martínez-Miranda<sup>a</sup>, Pablo Cañizares<sup>c</sup>, Ivonne Linares-Hernández<sup>a</sup>, Manuel A. Rodrigo<sup>c,\*</sup>

<sup>a</sup> Centro Interamericano de Recursos del Agua (CIRA), Universidad Autónoma del Estado de México, Facultad de Ingeniería, Unidad San Cayetano, km.14.5 Carretera, Toluca-Atlacomulco, C.P 50200, Toluca, Estado de México, Mexico

<sup>b</sup> Chemical Engineering Department, School of Industrial Engineering University of Castilla-La Mancha. Campus Universitario s/n, 02071 Albacete, Spain

<sup>c</sup> Chemical Engineering Department, Faculty of Chemical Sciences and Technologies, University of Castilla-La Mancha, Edificio Enrique Costa Novella.

Campus Universitario s/n, 13005 Ciudad Real, Spain

<sup>d</sup> Instituto Nacional de Investigaciones Nucleares (ININ), Departamento de Química, Carretera México-Toluca S/N, La Marquesa, C.P. 52750, Ocoyoacac, Estado de México, Mexico

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## ABSTRACT

This work describes the treatment of soil polluted with the herbicide pendimethalin by the combination of surfactant-aided soil-washing (SASW) and electrochemical advanced oxidation processes. Results show that it is possible to completely extract the herbicide from soil using SDS (sodium dodecyl sulfate) solutions as soil washing fluid (SWF) and ratios SWF/soil higher than  $10 \text{ dm}^3 \text{ kg}^{-1}$ . Soil washing effluents obtained after the application of the SASW consisted of a mixture of surfactant (high concentration) and pesticide (low concentration) and their degradation by electrolysis, photo-assisted electrolysis (photoelectrolysis) and sonochemistry with diamond anodes has been compared with that obtained by the application of single photolysis and sonolysis. Opposite to photolysis and sonolysis, the different electrolytic techniques allow decreasing the concentration of herbicide and surfactant in the effluents. Competition between the surfactant and the herbicide oxidation is important and irradiation of high-frequency ultrasound or UV light do not seem to outperform very importantly the results obtained by single electrolysis in the effluents of the SASW obtained with low SDS/soil ratios. Opposite, photoelectrolysis becomes the most efficient technology for the treatment of SWF obtained at high SDS/soil ratios (those required for an efficient SASW). Catalytic effect of the sulfate released during the degradation of SDS (in particular the formation of sulfate radicals) can help to explain the differences observed. The removal efficiency is higher during sonochemistry, reaching a final removal of the pesticide after 8 h of treatment of 86.22%. Photoelectrolysis (57.59%) shows higher efficiencies for the removal of SDS followed by sonochemistry (52.64%) and, finally, electrolysis (48.29%), after 8 h of treatment.

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## 1. Introduction

Over the last seventy years, the increasing use and the hazardousness of organic pesticides has alarmed to environmental authorities which, in turn, have favor the application of a stricter regulation about the manufacturing and application of these agro-

chemicals. Nowadays, many products, which have been widely applied for decades, are banned in many countries and there is an important search of technologies capable to minimize the impact of the pesticides which are still in use, in order to control their diffusion and to minimize their negative impacts on human health and environment.

Among pesticides, herbicides are able to rapidly remove the weed of crops. They have to be applied in large concentrations and the interaction with the soil matrix may be important. For this reason, their presence is not only limited to soils but they can also be present in groundwater in significant concentrations. Further-

\* Corresponding author.

E-mail addresses: [manuel.rodrigo@uclm.es](mailto:manuel.rodrigo@uclm.es), [mandres.rodrigo@gmail.com](mailto:mandres.rodrigo@gmail.com) (M.A. Rodrigo).

more, these compounds can be found in soils because of accidental discharges and, in this case, the concentration of herbicides can be much higher than that found from agricultural activities. Hence, it is necessary to develop clean and efficient technologies that allow an efficient removal of these compounds from both, soil and water.

One of the most applied technologies for the treatment of different pollutants from soils is soil washing, which is considered as an excellent technique due to its simplicity and high efficiencies reached in the removal of various types of pollutants [1–3]. This process consists of a physical treatment, where the pollutant is transported from soil to a liquid stream, commonly called Soil Washing Fluid (SWF). To obtain high efficiencies with this technology, it is essential to attain an efficient mass transfer of the pesticide from soil to the liquid stream and, in the case of pollutants with low solubility in water, it can be needed the use of surfactants during the treatment and this process is known as SASW, Surfactant-Aided Soil-Washing [4,5]. Anyhow, the outcome of soil washing technology is a treated soil and a highly-polluted soil washing fluid, which needs for additional treatment.

Electrochemical processes are among the most promising technologies for the treatment of soil washing effluents polluted with organics [6–10]. Specifically, electrolyses with diamond electrodes have been proven efficient in the removal of different types of pollutants from wastewater, reaching a total mineralization of the organic matter [11–16]. This technology is based on the generation of powerful oxidants from the oxidation of the ions naturally contained in wastewater [17]. Likewise, diamond anodes favor the generation of large amounts of hydroxyl radicals during wastewater treatment which, in turn contribute to the mineralization of the organic matter [18]. Nonetheless, the main drawback of the electrolytic technology is the mass transfer limitations associated to the transport of the pollutant to the anode surface. For this reason, to overcome this limitation, the electrochemical oxidation can be coupled with other processes such as US (sonoelectrolysis) and UV light irradiation (photoelectrolysis) [19,20]. In this context, the use of ultrasound waves or UV light may promote the activation of the oxidants electrogenerated, favoring the formation of free radicals. These species significantly contribute to the mineralization of the organic matter [21–23].

One of the most commonly-used herbicides is pendimethalin ( $C_{13}H_{19}N_3O_4$ ). This is a nitro-organic compound that allows preventing the growth of weeds in different crops such as garlic, artichoke, cotton, barley and onion. However, this compound can promote different types of cancer in humans and, therefore, should be removed from water [24]. Despite its extended application, there are few works in literature related to its degradation. Thus, Pinto et al. [25] studied the removal of pendimethalin by fungi cultures. They described the application of different fungi for the biodegradation of pendimethalin showing that *Lecanicillium saksenae* (*L. saksenae*) could remove 99.5% of the chemical in batch liquid cultures. Another study was carried out by Fenoll et al. [26], who described the photodegradation of pendimethalin in drinking water at pilot plant scale. They proposed the use of the ZnO catalyst for the removal of the pesticide, reaching a final concentration lower than  $0.8 \mu\text{g dm}^{-3}$ . More recently, Ahammed Shabeer et al. [27] carried out the removal of pendimethalin by a combined adsorption-coagulation-flocculation using aluminum and polyaluminum chloride as coagulants and modified montmorillonites and bentonite as adsorbents. They demonstrated that the combined treatment was much more efficient than single processes. Thus, this combined technology allowed removing higher than 90% of the herbicide.

Nevertheless, its treatment by electrochemical technology has not been reported and, in addition, the literature only includes the degradation of the herbicide in water but not in soils, where the impact can even be higher. Taking into account this background,

the main aim of the present work is to evaluate the application of a combined soil washing-electrolysis treatment for the removal of pendimethalin from spiked soil. The influence of the ratio surfactant/soil has been studied during soil washing and electrolysis because it seems to have a clear influence in the kinetics and the removal efficiency. Furthermore, in order to try to improve the process performance, the coupling of US and UV light irradiation to the electrochemical process (sonoelectrolysis and photoelectrolysis, respectively) was evaluated during the electrochemical treatment.

## 2. Material and methods

### 2.1. Chemicals

Pendimethalin (3,4-dimethyl-2,6-dinitro-N-pentan-3-ylaniline) and sodium dodecyl sulfate (SDS) (Sigma-Aldrich, Spain) were analytical grade and used as received. Acetonitrile HPLC grade (Sigma-Aldrich, Spain) was used for the mobile phase. Sodium tetraborate decahydrate, sodium hydroxide, phenolphthalein, methylene blue and chloroform (Sigma-Aldrich, Spain) were used for the determination of surfactant. Sodium carbonate and acetone (Sigma-Aldrich, Spain) were used as mobile phase for the determination of sulfate. Double deionized water (Millipore Milli-Q system, resistivity:  $18.2 \text{ M}\Omega \text{ cm}$  at  $25^\circ\text{C}$ ) was used to prepare all solutions.

### 2.2. Analytical techniques

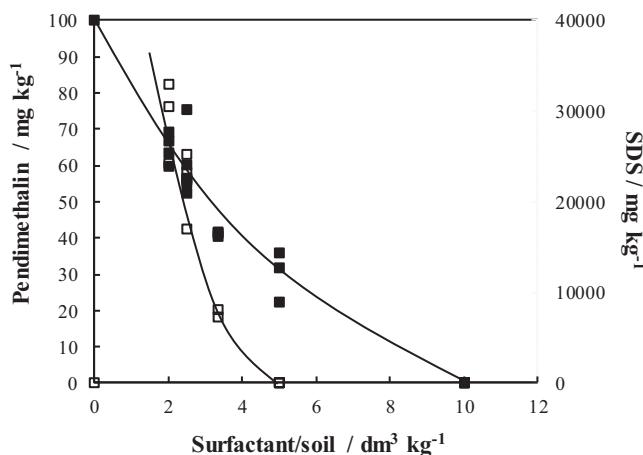
Samples were filtered with  $0.22 \mu\text{m}$  nylon filters Scharlau provided by Scharlab. The concentration of pendimethalin was followed by reversed-phase chromatography. A L-L extraction was carried out before analytical analysis. The herbicide was extracted from water using ethyl acetate (1:1 v/v) in Eppendorf tubes ( $15 \text{ cm}^3$ ) at 4000 rpm. The chromatography system was an Agilent 1200 series coupled a DAD detector. A ZORBAX Eclipse Plus C18 analytical column was used. The mobile phase consisted of 85:15 acetonitrile/water (flow rate:  $0.8 \text{ cm}^3 \text{ min}^{-1}$ ). The DAD detection wavelength was 240 nm, the temperature was maintained  $25^\circ\text{C}$  and the injection volume was  $20 \mu\text{L}$ . The TOC concentration was monitored using a Multi N/C 3100 Analytik Jena analyzer. Particle size was measured using a Mastersizerhydro 2000SM (Malvern) and SDS concentration was monitored with the colorimetric method reported by Jurado et al. [28]. Sulfate concentration was measured by ion chromatography using a Metrohm 930 Compact IC Flex coupled to a conductivity detector. A Metrosep A Supp 7 column was used for the determination. The mobile phase consisted of 85:15 v/v  $3.6 \text{ mM Na}_2\text{CO}_3$ /acetone with a flow rate of  $0.8 \text{ mL min}^{-1}$ . The temperature of the oven was  $45^\circ\text{C}$  and the volume injection was  $20 \mu\text{L}$ . The concentration of persulfate was determined iodometrically according to Kolthoff & Carr [29] and Standard methods [30].

### 2.3. Preparation of spiked soil

To pollute soil, pendimethalin was solubilized in hexane (solubility in water:  $0.3 \text{ mg dm}^{-3}$ ) and the solution was sprayed to clay soil. The main characteristics of the soil have been reported elsewhere [31]. Then, soil was aerated for 1 day to evaporate the solvent used (hexane). Thus, the pesticide was homogenously distributed in soil with an average concentration of  $100 \text{ mg kg}^{-1}$ .

### 2.4. Preparation of soil washing effluents

Soil washing was carried out in a stirred tank and discontinuous mode, by mixing different ratios between volumes of SWF



**Fig. 1.** Concentration of pendimethalin (■) and SDS (□) in soil as function of ratio volume SWF/soil mass after SASW process. Concentration of the SFW used: 20  $\text{g dm}^{-3}$  of SDS.

(soil washing fluid) and amounts of spiked soil (ranging between 0.1–0.5 kg). The SWF consisted of a solution of surfactant SDS in different concentrations (5–50  $\text{g dm}^{-3}$ ). Both phases (washing fluid and soil) were mixed for 12 h at 150 rpm. Then, the same tank was used as settler to separate the phases (24 h). The resulting effluents were aqueous mixtures of pendimethalin/surfactant micelles and soluble species. The concentration of herbicide was within the range 10–30  $\text{mg dm}^{-3}$ .

## 2.5. Electrochemical cell

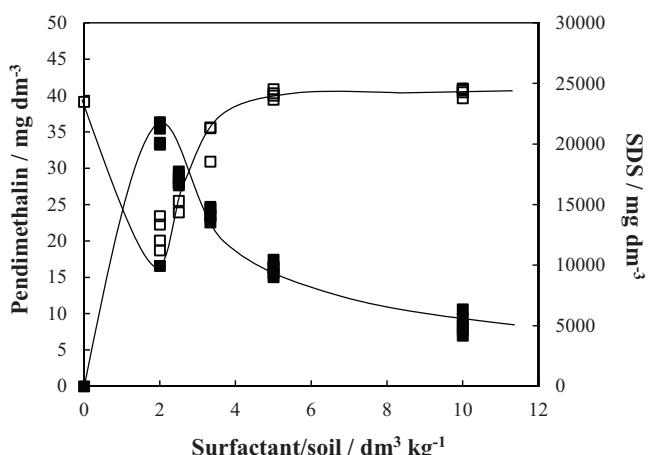
Electrolyses were carried out in a single compartment electrochemical flow cell. Boron doped diamond (BDD) with a geometric area of 78  $\text{cm}^2$  (WaterDiam, Switzerland) was used as anode and stainless steel (SS) as cathode. To allow the irradiation of UV light inside the electrochemical cell, the cathode material consisted of a grid and one of the cell covers was made of quartz. The inter-electrode gap between both electrodes was 9 mm. A low pressure Hg vapor UV lamp VL-215MC (Vilber Lourmat),  $\lambda = 254 \text{ nm}$ , intensity of 930  $\mu\text{W/cm}^2$  and energy 4.89 eV irradiated 4 W directly to the quartz cover. A high-frequency ultrasound (Epoch 650 ultrasound horn, Olympus) was used to provide waves into the system at 10 MHz. The power of ultrasound was 200 W. A Delta Electronika ES030-10 power supply (0–30 V, 0–10 A) provided the electric current. Wastewater was stored in a glass tank (0.6  $\text{dm}^3$ ). BDD anode presents a boron concentration of 500  $\text{mg dm}^{-3}$ , a thickness of 2.72  $\mu\text{m}$ ,  $\text{sp}^3/\text{sp}^2$  ratio of 220 and p-Si as support.

Experiments were carried out under galvanostatic conditions (30  $\text{mA cm}^{-2}$ ) and discontinuous mode. Samples (0.025  $\text{dm}^3$ ) were collected in the glass tank and persulfates were measured immediately. The influence of the ratio SDS/soil was studied on the electrochemical removal of the herbicide.

## 3. Results and discussion

### 3.1. Treatment of soil by SASW

In order to evaluate the efficiency of the soil washing in the removal of pendimethalin, several SASW tests were carried out to treat spiked soils with 100  $\text{mg kg}^{-1}$  of herbicide, using different surfactant/soil ratios. Fig. 1 shows the concentration of pendimethalin and SDS that remains in the soil after the application of the SASW process and Fig. 2 informs about the quality of the soil washing effluent produced in each of these tests.



**Fig. 2.** Concentration of pendimethalin (■) and SDS (□) in the washing fluid as function of ratio surfactant/soil after SASW process.

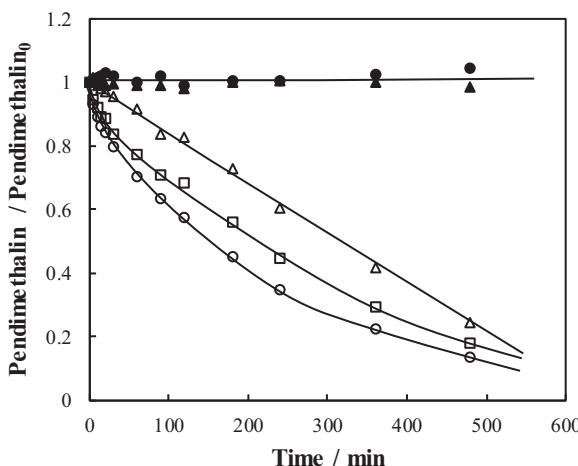
From Fig. 1, it can be stated that the herbicide is completely exhausted from the soil and released to the liquid phase from ratios SWF/soil higher than 10  $\text{dm}^3 \text{ kg}^{-1}$  (which taking into account the concentration of 20  $\text{g dm}^{-3}$  of SDS used in the SWF, means 200  $\text{g SDS kg}^{-1}$  soil) and the removal efficiency is clearly influenced by this ratio so, the higher the dose, the higher is the resulting removal of herbicide from soil. This very high-dose of SDS required should be explained in terms of the rather low solubility of the pesticide in water, associated to its non-polar character. Likewise, it is related to the high octanol/water partition coefficient of the herbicide, inducing a great adsorption on that soil.

Fig. 2 focuses on the quality of the soil washing waste produced in each of the tests by showing the concentration of pendimethalin and SDS in the different liquid wastes produced during the application of SASW at different surfactant/soil ratios.

As it can be seen, the main pollutant in the waste (in terms of concentration) is not the herbicide but the surfactant, because the SDS concentration required for an efficient remediation of the soil is much higher than the extracted concentration of herbicide (which is only of few  $\text{mg dm}^{-3}$ ). Hence, the resulting effluent of the SASW process consists of a dispersion with low concentration of pendimethalin and a much higher concentration of SDS, with at least three different pollutant species: soluble pendimethalin, soluble SDS and micelles pendimethalin-SDS. The high pollution of this SWF corresponds to the high organic load associated to SDS, although the hazardousness is related not to the surfactant but to the presence of the herbicide. The retention of the SDS in the soil when high amounts of soil are washed is reflected in the quality of the effluent produced. Regarding the lower concentration of pendimethalin at higher SDS/soil ratios, it is a consequence of the dilution caused by the use of higher volumes of SWF. As it can be figured out from results shown in Fig. 1, the total amount of pendimethalin contained in this waste increases with the SDS/soil ratio as the herbicide is fully extracted from soil.

### 3.2. Treatment of soil washing effluents by different oxidation technologies

Once SASW has been confirmed as an appropriate technology for removal of pendimethalin from soils, this technology was applied to treat 10.0 kg of spiked soil (with a surfactant/soil ratio of 10  $\text{dm}^3 \text{ kg}^{-1}$ ) and the resulting soil washing effluent (60  $\text{dm}^3$ ) was treated by different technologies based on the electrolysis with diamond anodes, as well as with other non-electrochemical advanced oxidation processes. This allows us to determine the technology that exhibit the best characteristics for the treatment of

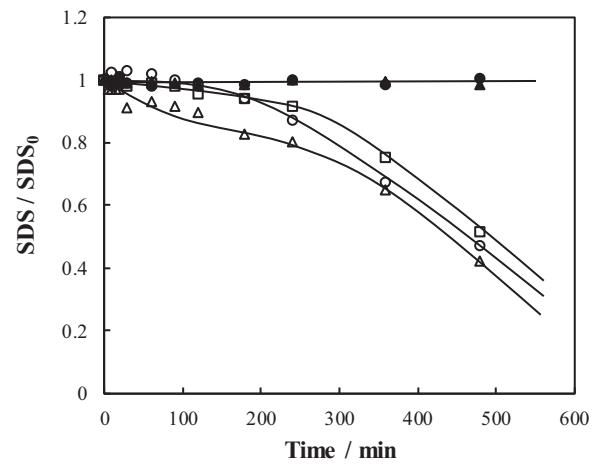


**Fig. 3.** Evolution of pesticide concentration as function of the operation time during the treatment of soil washing effluents. SDS/soil: 200 g kg<sup>-1</sup> (10 dm<sup>3</sup> kg<sup>-1</sup>). (□) electrolysis; (▲) photolysis; (△) photoelectrolysis; (●) sonolysis; (○) sonoelectrolysis. j: 30 mA cm<sup>-2</sup>; W<sub>UV254nm</sub>: 4 W; W<sub>US10MHz</sub>: 200 W.

these SASW effluents polluted with pendimethalin. According to recent works, in many cases the efficiency of the electrolysis with diamond electrodes can be enhanced simply by applying high-frequency ultrasounds or irradiating ultraviolet light to the bulk of the solution, because this irradiation assists in the formation of radicals from the oxidants electrogenerated on the anode and cathode surface of the electrochemical cell. It is important to point out that the effluents of the SASW process were treated as produced and no salts were added to improve the conductivity (2–3 mS cm<sup>-1</sup>). At this point, it is important to take in mind that salt addition is not a good practice and should be avoided in the development of environmental applications because it leads to a less hazardous but more persistent pollution in the liquid wastes.

Taking into account these remarks, Fig. 3 compares the evolution of pendimethalin with the operation time during the electrolytic, sonolytic, sonoelectrolytic, photolytic and photoelectrolytic treatment of soil washing effluents.

As it can be observed, there are no remarkable changes in the concentration of the herbicide during single sonochemical and photochemical processes, which indicates that sonolysis and photolysis are not suitable technologies for the degradation of pendimethalin in soil washing wastes. The small differences may be related to the accuracy of the analytical technique, because there is no a clear decrease trend. On the other hand, the concentration of herbicide decreases with the operation time during the electrolytic and electro-irradiated processes. The removal efficiency is higher during sonoelectrolysis, reaching a final removal of the pesticide after 8 h of treatment of 86.22%. In the case of electrolysis and photoelectrolysis, the final removal percentage is 81.88 and 75.32%, respectively. Nonetheless, it is not possible to attain a complete removal of pendimethalin within the electrolysis time used, regardless the technology used. This is an unexpected behavior considering that, according to the results shown in most of the works found literature, 8 h of electrolysis at 30 mA cm<sup>-2</sup> (passing more than 18.72 Ah) is more than enough to deplete such a low concentration of pollutant from only 1 dm<sup>3</sup> of liquid waste [31,32]. However, this fact must be related to the competitive oxidation between the pesticide and the surfactant, the other pollutant contained in the waste. In this context, it is important to point out that the concentration of SDS in the SWF was 20 g dm<sup>-3</sup>, whereas the pesticide concentration is only about few mg dm<sup>-3</sup>. Therefore, the electrochemical oxidation of SDS may be promoted instead of the removal of pesticide, simply because the concentration of SDS

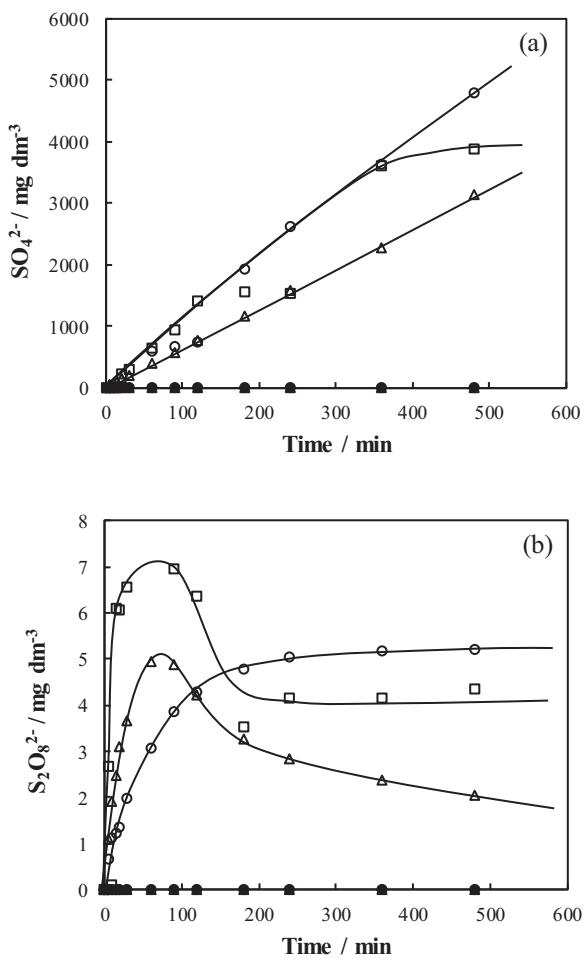


**Fig. 4.** Evolution of surfactant concentration as function of the operation time during the treatment of soil washing effluents. SDS/soil: 200 g kg<sup>-1</sup> (10 dm<sup>3</sup> kg<sup>-1</sup>, 20 g dm<sup>-3</sup> SDS). (□) electrolysis; (▲) photolysis; (△) photoelectrolysis; (●) sonolysis; (○) sonoelectrolysis. j: 30 mA cm<sup>-2</sup>; W<sub>UV254nm</sub>: 4 W; W<sub>US10MHz</sub>: 200 W.

is several log-units above the concentration of pendimethalin. To check this possibility, the concentration of surfactant was monitored during the tests. Fig. 4 shows the evolution of SDS with the operation time during the degradation of pendimethalin.

As for the herbicide, the concentration of SDS remained almost constant during single US and UV irradiation processes. Conversely, surfactant concentration decreases significantly with the time during the application of the electrochemical technologies. In this case, two different trends can be clearly discerned. First, surfactant slightly decreases during the process until reaching an operation time of about 250 min from which the elimination rate significantly increases. These results may reveal a competitive oxidation between the pesticide and surfactant during the electrochemical processes. In fact, the pesticide removal rate follows an opposite behavior: there is an initial rapid degradation of pendimethalin (until 250 min) and then, the elimination rate decreases (corresponding to the rapid degradation of the surfactant). Alternatively, the faster and more efficient removal of SDS may be related to the release of sulfate and its role as precursor in the formation of peroxosulfates, which may have a great influence on the removal of SDS catalyzing it. This release is going to be described later in this work. Anyhow, although both explanations can support the experimental observations, this second explanation seems to fit it better, because of the huge differences between the concentrations of SDS and herbicide that hardly may support a competitive oxidation from the viewpoint of SDS removal.

The efficiency of the surfactant degradation depends importantly on the technology used. In this context, photoelectrolysis shows higher efficiencies for the removal of SDS followed by sonoelectrolysis and, finally, electrolysis. Specifically, after 8 h of treatment, a surfactant removal percentage of 57.59, 52.64 and 48.29% was attained during photoelectrolysis, sonoelectrolysis and electrolysis, respectively. This fact can be related to the role of oxidants during electrochemical processes. In this context, SDS contains a sulfate group in its structure which can be released during the degradation process [33]. These sulfate ions can be oxidized during the treatment, favoring the production of peroxosulfates (Eq. (1)). Likewise, the production of large amounts of hydroxyl radicals can take place by water oxidation during electrolysis with diamond anodes (Eq. (2)) [18]. These radicals contribute to the degradation of both pesticide and surfactant but also, they can react



**Fig. 5.** Changes in sulfate (a) and persulfate (b) concentration as function of the operation time during the treatment of soil washing effluents. SDS/soil:  $200 \text{ g kg}^{-1}$  ( $10 \text{ dm}^3 \text{ kg}^{-1}$ ,  $20 \text{ dm}^{-3}$  SDS). (□) electrolysis; (▲) photolysis; (△) photoelectrolysis; (●) sonolysis; (○) sonochemical test.  $j: 30 \text{ mA cm}^{-2}$ ;  $W_{\text{UV}254\text{nm}}: 4 \text{ W}$ ;  $W_{\text{US}10\text{MHz}}: 200 \text{ W}$ .

with sulfate promoting the potential formation of persulfates (Eqs. (3)–(4)).



Furthermore, the irradiation of US and UV light promotes the activation of the electrogenerated oxidants, favoring the formation of free radicals (Eqs. (5)–(6)) which may significantly contribute to the degradation of the organic pollutants [21,34,35].



Taking into account these remarks, Fig. 5 shows the concentration of sulfate (a) and persulfate (b) during the different treatment tests of soil washing effluents polluted with pendimethalin. As it can be seen, sulfates increase with the operation time reaching final concentrations higher than  $3000 \text{ mg dm}^{-3}$ , regardless the electrolytic technology used. No release of sulfates was detected during single US and UV irradiation processes (Fig. 5a). This agrees to the previous results obtained for the evolution of surfactant where SDS remains constant during the complete treatment (Fig. 4).

The production of sulfates is higher during the sonochemical test as compared with the values observed in other technologies. This can be related to the effect of ultrasounds throughout the process, because the high-frequency ultrasonic irradiation can significantly promote the breaking of the molecule of SDS [36,37].

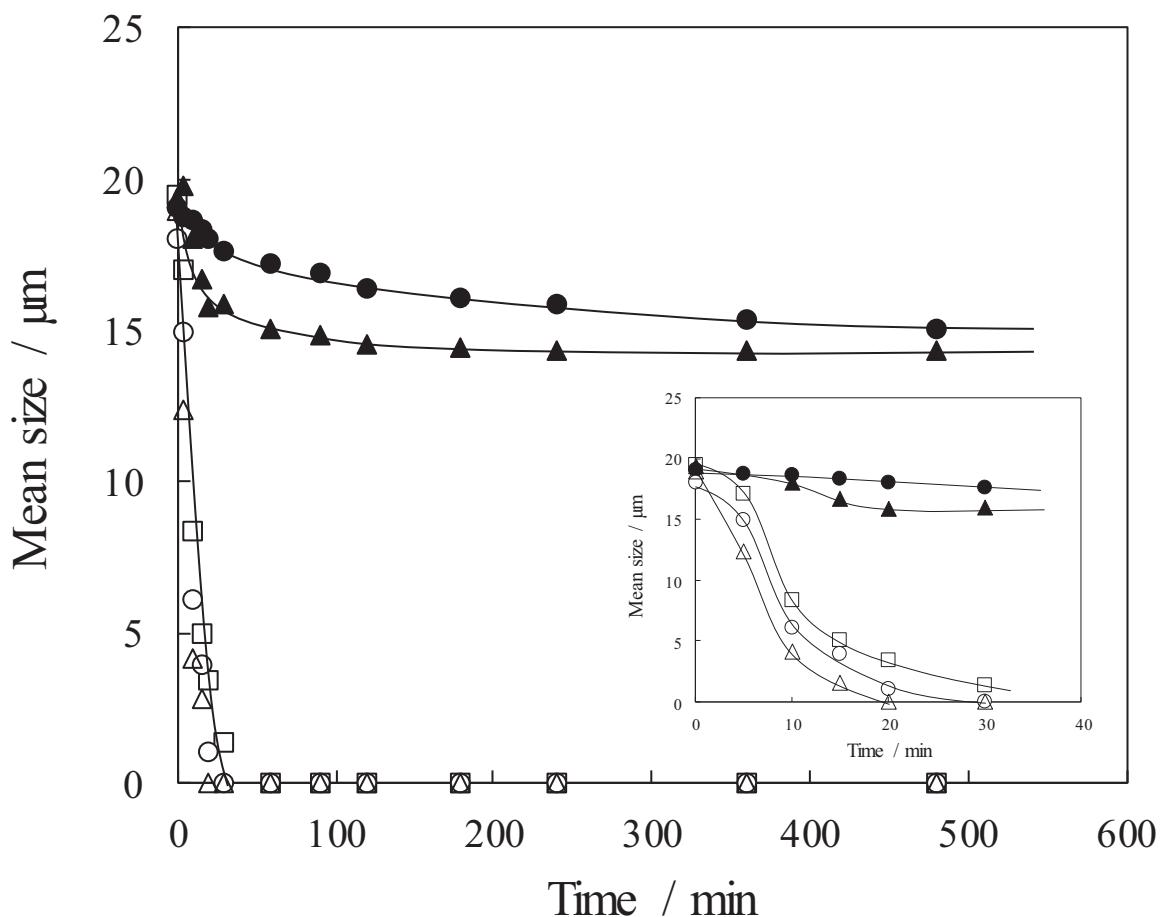
The concentration of peroxosulfate also increases during the different electrochemical treatments of soil washing effluents. However, this concentration is much lower than that of sulfate and it may be explained by taking into account that peroxosulfate is continuously reacting with the organic matter present in the effluent and, therefore, it is only possible to measure the concentration of persulfate that has not reacted. The trends observed indicate that a high consumption of these species takes place during the process. Nonetheless, different behaviors can be seen depending on the technology used.

The amount of peroxosulfate initially increases until 1 h, followed by a decrease during electrolysis and photoelectrolysis, being its concentration higher during the non-irradiated process. This higher concentration may be related to the photo-activation of peroxosulfate during photoelectrolysis. Furthermore, peroxosulfate remains constant at the end of electrolysis whereas decreases continuously during photo-electrolysis. This indicates that the generation and consumption rates are similar during the last minutes of electrolysis. The same behavior is observed during the treatment of soil washing effluents by sonochemical test where the concentration of peroxosulfate increases until reaching a value from which it remains constant. Finally, it is important to point out that the final concentration of peroxosulfate is higher during sonochemical test, which can be associated to a higher removal of SDS and thus to the higher concentration of sulfate contained in the effluent (Fig. 5a). One important comment that should be pointed out is the increase in the oxidation rate of SDS at long electrolysis times (Fig. 4), which may be alternatively explained by the mediated oxidation produced by the presence of larger concentrations of peroxosulfates in the solution.

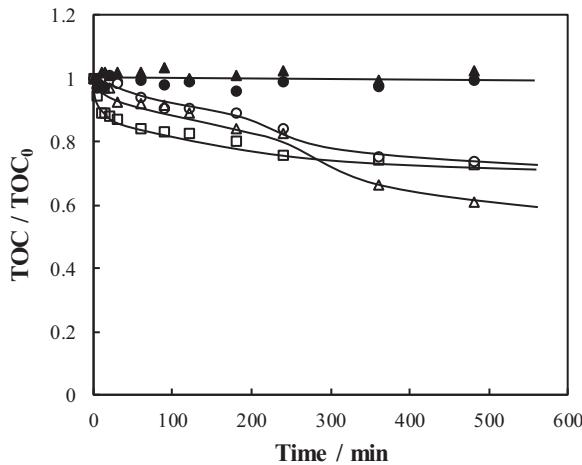
As pointed out before, the soil washing effluent consists of a mixture of three species. Results discussed up to now refers to total concentrations of surfactant and herbicide but it is important to note that they are contained in the waste in three different species: soluble herbicide, soluble surfactant and micelles. Hence, to obtain more information about the removal of pendimethalin in soil washing effluents, it is important to study the behavior of the emulsions pesticide/surfactant during the treatment and, to assess the breakup of emulsions and the subsequent reduction of micelles [38]. For this reason, the particle size was monitored during the treatment. Fig. 6 shows the evolution of particle size during the treatment of soil washing effluents polluted with pendimethalin by different technologies.

Particle size slightly decreases with the operation time during single US and UV irradiation processes, remaining constant at the end of the experiments. Hence, despite no oxidation was observed with these non-electrochemical technologies, irradiation of high frequency ultrasounds or UV light produce an appreciable but limited effect on the size of the micelles. On the contrary, this parameter reaches zero values during electrochemical processes after only 1 h. This indicates that the concentration of micelles decreases rapidly. Likewise, photoelectrolysis leads to a faster decrease in the particle size followed by sonochemical test and electrolysis, respectively. In fact, particle size reaches zero values at operation time of only 20 min whereas sonochemical test requires 30 min and electrolysis 1 h to deplete completely micelles. This agrees with the previous data obtained in the removal of SDS, where photoelectrolysis showed the higher degradation efficiency (Fig. 4).

The oxidation of pendimethalin and SDS can lead to a complete mineralization of the organic matter to carbon dioxide or to the formation of other intermediate organic compounds. These last ones



**Fig. 6.** Changes in particle size as function of the operation time during the treatment of soil washing effluents. SDS/soil:  $200 \text{ g kg}^{-1}$  ( $10 \text{ dm}^3 \text{ kg}^{-1}$ ,  $20 \text{ g dm}^{-3}$  SDS). (□) electrolysis; (▲) photolysis; (△) photoelectrolysis; (●) sonolysis; (○) sonoelectrolysis. j:  $30 \text{ mA cm}^{-2}$ ;  $W_{\text{UV}254\text{nm}}: 4 \text{ W}$ ;  $W_{\text{US}10\text{MHz}}: 200 \text{ W}$ .



**Fig. 7.** Evolution of TOC as function of the operation time during the treatment of soil washing effluents. SDS/soil:  $200 \text{ g kg}^{-1}$  ( $10 \text{ dm}^3 \text{ kg}^{-1}$ ,  $20 \text{ g dm}^{-3}$  SDS). (□) electrolysis; (▲) photolysis; (△) photoelectrolysis; (●) sonolysis; (○) sonoelectrolysis. j:  $30 \text{ mA cm}^{-2}$ ;  $W_{\text{UV}254\text{nm}}: 4 \text{ W}$ ;  $W_{\text{US}10\text{MHz}}: 200 \text{ W}$ .

can be more hazardous than the initial pollutants and, therefore, they should be removed from effluents. To shed light about the mineralization of the organic matter, the concentration of TOC was monitored during the tests. This parameter provides information about the percentage of mineralization of the organic matter during the treatments. Results are illustrated in Fig. 7.

As expected, TOC concentration remains constant during single US and UV irradiation processes indicating again that single photolysis and sonolysis are not enough for the treatment of these wastes. However, this parameter decreases during the electrochemical experiments, although it is not possible to attain a complete mineralization of the organic matter within the electrolysis time applied (8 h). Specifically, these technologies attain a percentage removal of about 27% (electrolysis: 27.6%; sonoelectrolysis: 26.51%) whereas photoelectrolysis leads to a final mineralization of the organic matter of 39.04%. Single electrolysis is the most efficient technology for the mineralization of the organic matter in the first stages of the process. This reveals that the application of UV light or US irradiation does not significantly improve the mineralization attained with single electrolysis during the treatment of high concentrated surfactant solutions.

In comparing the changes observed for the degradation of the different species contained in the soil washing wastes, it seems clear that irradiation of high-frequency US and UV light influences significantly on the results of the electrolysis with diamond. High-frequency US seems to improve the degradation of pendimethalin as compared with single electrolysis and photoelectrolysis, but it has a negative impact on the degradation of SDS. The opposite trend is observed for photoelectrolysis, which clearly enhances the oxidation of SDS as compared to single electrolysis and sonoelectrolysis. As SDS is the main pollutant contained in the soil washing effluent (both as soluble species and also as surface of the micelles), this better prospects of the UV irradiation makes photoelectrolysis the most suitable technology for the treatment soil washing efflu-

ents obtained from the SASW at very high surfactant/soil ratios. In fact, this technology attains the more efficient TOC removal and the faster exhaustion of the micelles. The UV-light activation of persulfates to form sulfate radicals (reflected in a lower concentration of persulfates as compared to the other technologies tested) is the most plausible way to explain these observations.

### 3.3. Effect of the quality of the SASW effluent on the performance of the oxidation technologies evaluated

Results shown in the previous section focuses on the treatment of an effluent of the SASW process with an extremely high SDS concentration, because the ratio surfactant/soil applied in the SASW process was high enough to exhaust all the herbicide contained in soil.

In some cases, these extreme conditions are not necessary to be applied and hence effluents with more favorable SDS/pendimethalin ratio are produced. In order to clarify the differences produced by these different characteristics of the effluent, several soil washing effluents were obtained by washing soils with different SDS/soil ratios. As the general remarks about the treatment of these effluents were discussed in Section 3.2, now discussion is going to be focused only on the comparison of the kinetic constants obtained for the removal of pendimethalin, SDS and TOC as function of different ratios SDS/soil. These kinetic constants were calculated by fitting experimental data to first order kinetic model and are plotted vs the SDS/soil ratio in Fig. 8.

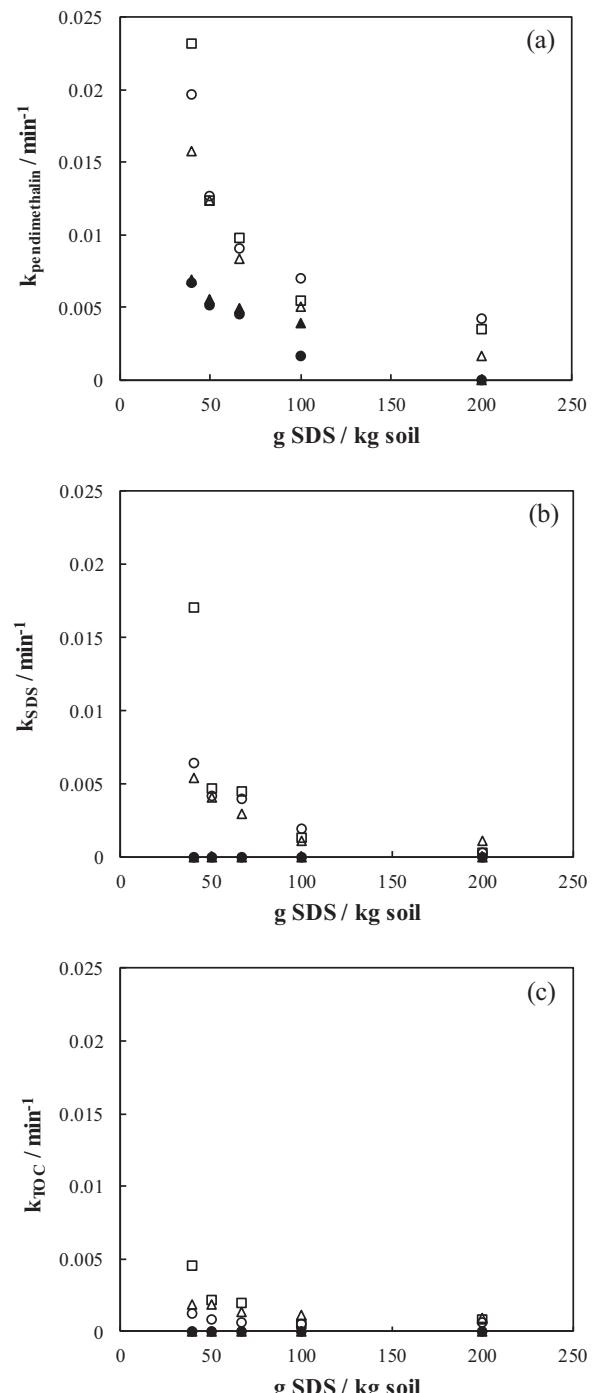
Overall, the kinetic constant for all parameters increases when the ratio SDS/soil decreases (pesticide, surfactant and TOC) regardless the technology used. Again, single photolysis and sonolysis demonstrate to be not suitable technologies for the removal of the herbicide and SDS.

The removal of pendimethalin is more efficient during sonoelectrolysis when working at SDS/soil ratios higher than 100 g kg<sup>-1</sup>. At low ratios (less than 66.67 g kg<sup>-1</sup>), electrolysis shows higher efficiencies. Photoelectrolysis seems to be the less suitable technology for the removal of pendimethalin, regardless the ratio SDS/soil. However, it is important to point out that the difference with electrolysis and sonoelectrolysis are more remarkable at low ratios (40 g kg<sup>-1</sup>). This behavior is related to the physical-chemical properties of each effluent. In this context, low SDS/soil ratios mean that higher mass of soil has been washed with the same amount of SDS added and, therefore, the particles size is higher, hindering an efficient irradiation of UV light on the electrogenerated oxidants and a subsequent efficient pendimethalin removal.

Regarding kinetic constants observed for the removal of SDS (Fig. 8b), electrolysis follows the same trend than that observed during herbicide removal: the efficiency is higher when working at low SDS/soil ratios. On the other hand, at 200 g kg<sup>-1</sup>, photoelectrolysis shows the higher efficiency due to the enhanced formation of free sulfate radicals inside the electrochemical cell by the effective irradiation of UV light (low mass of soil). Nonetheless, from values higher than 100 g kg<sup>-1</sup>, this technology shows the lower efficiency in comparison with electrolysis and sonoelectrolysis. In addition, it is important to remark that the kinetic constants calculated for surfactant removal are lower than that obtained during the degradation of pendimethalin. This is related to the lower efficiency of SDS removal in comparison with the pesticide removal.

Finally, a similar behavior can be observed for the TOC (which informs about the total mineralization of the organic matter) (Fig. 8c). However, photoelectrolysis shows higher efficiencies than sonoelectrolysis for the removal of TOC, regardless the ratio SDS/soil. This fact suggests that the formation of intermediates is more favored during sonoelectrolysis.

In comparing the effect to the surfactant/soil ratio on the global results attained by the different technologies tested, it is important



**Fig. 8.** Kinetic constants calculated for the removal of pesticide, surfactant and total organic carbon as function of the initial ratio surfactant/soil. (□) electrolysis; (▲) photolysis; (△) photoelectrolysis; (●) sonolysis; (○) sonoelectrolysis.

to note that performance is completely different at high and low values of the ratio. While at high values of the ratio, the enhanced degradation of SDS by the UV activation of sulfate radicals advice the use of photoelectrolysis, for low ratios, irradiation of US or UV does not attain any improvement but even they exhibit an antagonistic effect as compared to single electrolysis [39]. Lower concentration of persulfates, associated to the slower oxidation of SDS, can help to explain this worse performance.

Hence, results obtained in this work reveal that it is possible to remove the herbicide pendimethalin from soil washing effluents but the very high concentration of surfactant SDS required for an

efficient extraction, is the major source of organic pollution and it controls the performance of the electrolytic technology applied for the treatment of the soil washing waste. The important release of sulfates during the electrolysis at high SDS/soil ratios makes the photoelectrolysis the recommended SWF treatment technology for these effluents, while for effluents obtained at low SDS/soil ratios single electrolysis is the reference technology to be applied.

#### 4. Conclusions

From this work the following conclusions can be drawn:

- Pendimethalin can be extracted from soils by SASW using SDS as surfactant. Ratios SDS/soil higher than 200 g kg<sup>-1</sup> ensure a complete extraction of the herbicide.
- Electrolysis with diamond anodes of soil washing effluents polluted with pendimethalin allows decreasing the pesticide concentration in the effluent. However, the removal efficiency in the removal of pendimethalin is limited by the competitive oxidation between the herbicide and the surfactant.
- The oxidation of SDS leads to the release of sulfate ions in the effluent. These species are oxidized, favoring the production of persulfates which are the main responsible species of the degradation process.
- The ratio SDS/soil significantly influences the efficiency of electrolytic technologies. For high values of the SDS/soil ratio, irradiation of UV light improves the efficiency of the electrolytic technology because of the enhanced degradation of the SDS. At low SDS/soil ratios coupling of US or UV light irradiation to electrolysis with diamond anodes does not improve the process performance.

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